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December 21, 2001

**BOX PCT**

Commissioner for Patents  
Washington, D.C. 20231

PCT/FR00/01711  
-filed June 21, 2000

Re: Application of Jean-Pascal PLANCHE, Patrick TURELLO, Pierre CHAVEROT and  
Patrice VEGNY  
METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR FUNCTIONALIZED  
BITUMEN/POLYMER COMPOSITIONS AND USE OF SAID COMPOSITIONS IN  
COVERINGS  
Assignee: **ELF ANTAR FRANCE**  
Our Ref: Q67797

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

**The Declaration and Power of Attorney, English translation of the International Application and Assignment will be submitted at a later date.**

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

Total claims	<u>22</u>	-	20	=	<u>2</u>	x	\$18.00	=	<u>\$36.00</u>
Independent claims	<u>1</u>	-	3	=	<u></u>	x	\$84.00	=	<u>\$0.00</u>
Base Fee									<u>\$890.00</u>

**TOTAL FEE**

\$926.00

A check for the statutory filing fee of \$926.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Country

Application No

Filing Date

France

99/07914

June 22, 1999

Respectfully submitted,

Mark Boland

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MXB/slb

1001877900102  
78/018790  
Rec'd PCT/PTG 01 OCT 2002

**PATENT APPLICATION**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of

Docket No: Q67797

Jean-Pascal PLANCHE, et al.

Appln. No.: 10/018,790

Group Art Unit: Unknown

Confirmation No.: 1942

Examiner: Unknown

Filed: December 21, 2001

For: METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR  
FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE OF  
SAID COMPOSITIONS IN COVERINGS (as amended)

**PRELIMINARY AMENDMENT**

**ATTN: BOX PCT**  
Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-identified application as follows:

**IN THE TITLE:**

Please delete the present title and replace it with the following new title:

METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR  
FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE OF SAID  
COMPOSITIONS IN COVERINGS

**IN THE ABSTRACT:**

Please insert the Abstract on the attached separate page.

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**IN THE CLAIMS:**

**Please enter the following amended claims:**

1 (amended). A method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C and under agitation, forming a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix in which is uniformly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer used in a quantity that ranges between 0.5% and 30% of the weight of the bituminous matrix, where said method is characterized by making the bituminous matrix by associating, by weight, x% of a non oxidized bitumen with a penetrability that ranges between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined as set forth in NF standard T 66004 and are expressed in 1/10 mm, where the values of x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

2 (amended). The method as set forth in claim 1, characterized in that the weight percentages x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .

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3 (Amended). The method as set forth in claim 1, characterized in that the quantity of precursor elastomer represents from 1.5% to 20% of the weight of the bituminous matrix.

4 (Amended). The method as set forth in claim 1, characterized in that the non oxidized bitumen, entering in the making of the bituminous matrix, consists of one single bitumen or of a mixture of bitumens taken from among the straight-run bitumens, the refinery bitumens under reduced pressure, the propane or pentane deasphalting residues and viscosity breaking residues.

5 (amended). The method as set forth in claim 4, characterized in that the non oxidized bitumen is one bitumen or a mixture of bitumens taken from among the straight-run bitumens.

6 (Amended). The method as set forth in claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make up the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens taken from among the blown bitumens and the semi-blown bitumens.

7 (Amended). The method as set forth in claim 1, characterized in that the penetrability of the non oxidized bitumen, used in making the bituminous matrix, ranges between 35 and 500.

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8 (Amended). The method as set forth in claim 1, characterized in that the penetrability of the oxidized bitumen, used in making the bituminous matrix, ranges between 20 and 60.

9 (Amended). The method as set forth in claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make the bituminous matrix, has a ring and ball softening point as defined in the NF standard T 66008, that ranges between 60°C and 120°C.

10 (Amended). The method as set forth in claim 1, characterized in that the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene, namely butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene.

11 (amended). The method as set forth in claim 10, characterized in that the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene.

12 (Amended). The method as set forth in claim 10, characterized in that the copolymers of styrene and of conjugate diene have a styrene content that ranges between 5% and 50% by weight.

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13 (Amended). The method as set forth claim 10, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range between 10 000 daltons and 600 000 daltons.

14 (Amended). The method as set forth in claim 1, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% of the precursor elastomer and 0.01% to 6% of cross-linking agent and/or a functionalization agent while working at temperatures that range between 100°C and 230°C and under agitation for a period of time of at least 5 minutes.

15 (Amended). The method as set forth in claim 14, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 100°C and 230°C and under agitation for a period of time ranging from 5 minutes to 8 hours, to create a homogenous mixture, then the cross-linking agent and/or functionalization agent is incorporated into said mixture and it is all kept under agitation at temperatures ranging between 100°C and 230°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and the oxidized bitumens used to make the bituminous matrix, for a period of time that ranges

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between 5 minutes and 5 hours, to form a reaction product that makes up the cross-linked and/or functionalized bitumen/polymer composition.

16 (Amended). The method as set forth in claim 1, characterized in that it consists, in a first phase, in preparing a concentrate by putting from 50% to 100% of the non oxidized bitumen to be used to make the bituminous matrix in contact with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.01% to 6% of a cross-linking agent and/or a functionalization agent to form a cross-linked and/or functionalized bitumen/polymer reaction product that makes up said concentrate while working at temperatures ranging between 100°C and 230°C under agitation during a period of time of at least 5 minutes and then, in a second phase in diluting the cross-linked and/or functionalization bitumen/polymer reaction that resulted from the first phase and adding to it the oxidized bitumen and the possible remaining fraction of non oxidized bitumen, while operating at temperatures that range between 100°C and 230°C, under agitation, to form the cross-linked and/or functionalized bitumen/polymer composition.

17 (Amended). The method as set forth in claim 16, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 100°C and 230°C, and under agitation for a period of time from 5 minutes to 8 hours, to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or



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functionalization agent and holding it all under agitation at temperatures that range between 100°C and 230°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from 5 minutes to 5 hours, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

18 (Amended). The method as set forth in claim 14, characterized in that the functionalized elastomer is created within the bituminous matter using a functionalization agent selected from the group consisting of carboxylic acids or esters bearing thiol or disulfide groups and thiolcarboxylic acid polyesters.

19 (Amended). The method as set forth in claim 1, characterized in that the elastomer is functionalized and one or several reactive additives likely to react with the functional groupings of the elastomer are incorporated into the functionalized bitumen/polymer composition during its preparation where the quantity of the reactive additive(s) ranges from 0.01% to 10% of the weight of the bitumen present in the composition.

20 (Amended). The method as set forth in claim 14, characterized in that the cross-linked elastomer is created within the bituminous matrix, using a cross-linking agent selected from the group consisting of sulfur donor cross-linking agents and peroxidized compounds that generate free radicals at temperatures ranging between 100°C and 230°C.



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21 (Amended). The method as set forth in claim 1, further incorporating one or several additional polymers that are different from the precursor elastomer to the cross-linked and/or functionalized bitumen/polymer composition in an overall quantity that ranges between 0.3% and 20% of the weight of the bitumen of said compositions.

22 (Amended). A road surface pavement or a watertight facing made from a cross-linked and/or functionalized bitumen/polymer composition made from the method of claim 1.

**Please add the following new claims:**

23 (New). The method as set forth in claim 7, characterized in that the penetrability of the non oxidized bitumen, used in making the bituminous matrix, ranges between 160 and 330.

24 (New). The method as set forth claim 13, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range 30 000 daltons and 400 000 daltons.

25 (New). The method as set forth in claim 14, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 1.5% to 20% of the precursor elastomer and 0.05% to 3% of cross-linking agent and/or a

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functionalization agent while working at temperatures that range between 130°C and 200°C and under agitation for a period of time of at least 5 minutes.

26 (New). The method as set forth in claim 15, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 130°C and 200°C and under agitation for a period of time ranging from 30 minutes to 6 hours, to create a homogenous mixture, then the cross-linking agent and/or functionalization agent is incorporated into said mixture and it is all kept under agitation at temperatures ranging between 130°C and 200°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and the oxidized bitumens used to make the bituminous matrix, for a period of time that ranges between 10 minutes and 180 minutes, to form a reaction product that makes up the cross-linked and/or functionalized bitumen/polymer composition.

27 (New). The method as set forth in claim 16, characterized in that it consists, in a first phase, in preparing a concentrate by putting from 50% to 100% of the non oxidized bitumen to be used to make the bituminous matrix in contact with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.05% to 3%, of a cross-linking agent and/or a functionalization agent to form a cross-linked and/or functionalized bitumen/polymer reaction product that makes up said concentrate while working at temperatures ranging between 130°C and 200°C, under agitation

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during a period of time of at least 5 minutes and then, in a second phase in diluting the cross-linked and/or functionalization bitumen/polymer reaction that resulted from the first phase and adding to it the oxidized bitumen and the possible remaining fraction of non oxidized bitumen, while operating at temperatures that range between 130°C and 200°C, under agitation, to form the cross-linked and/or functionalized bitumen/polymer composition.

28 (New). The method as set forth in claim 17, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 130°C and 200°C, and under agitation for a period of time from 30 minutes to 6 hours, to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or functionalization agent and holding it all under agitation at temperatures that range between 130°C and 200°C and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from between 10 minutes and 180 minutes, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

29 (new). The method as set forth in claim 19, characterized in that the elastomer is functionalized and one or several reactive additives likely to react with the functional groupings of the elastomer are incorporated into the functionalized bitumen/polymer composition during its preparation where the quantity of the

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reactive additive(s) ranges from 0.05% to 5% of the weight of the bitumen present in the composition.

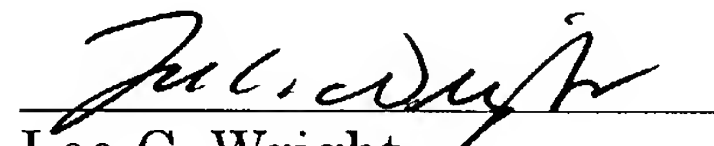
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REMARKS

The changes made to the claims are for clarity and to conform with U.S. claiming practice. New claims 23-29 correspond to the preferable subject matter of original claims 7, 13-17 and 19, respectively. Entry and consideration of this Amendment are respectfully requested.

Respectfully submitted,

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Lee C. Wright  
Registration No. 41,441

Date: October 1, 2002

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**APPENDIX**

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE TITLE:**

**The title is changed as follows:**

METHOD FOR THE PRODUCTION OF [PREPARING] CROSS-LINKED  
AND/OR FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE  
OF SAID COMPOSITIONS IN COVERINGS [THEIR APPLICATION IN THE  
MAKING OF PAVEMENTS]

**IN THE ABSTRACT:**

**The following was inserted on a separate sheet as the abstract:**

**ABSTRACT**

Compositions produced by forming a homogenous mass consisting of a  
bitumen matrix wherein a cross-linked and/or functionalized elastomer produced in  
situ from a precursor elastomer is dispersed in a uniform manner and makes up 0.5  
- 30% of the weight of the bitumen matrix. The bitumen matrix is created by  
associating 95 % - 20 wt. % non oxidized bitumen having a penetrability of 20-900  
and 5-80 wt. % oxidized bitumen having a penetrability of 10-90. The compositions  
can be used as bitumen binders in the production of coverings.

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**IN THE CLAIMS:**

**The claims are amended as follows:**

1 (amended). [- Method] A method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C and under agitation, [we form] forming a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix in which is uniformly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer used in a quantity that ranges between 0.5% and 30% of the weight of the bituminous matrix, where said method is characterized [in that we made] by making the bituminous matrix by associating, by weight, x% of a non oxidized bitumen with a penetrability that ranges between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined as set forth in the NF standard T 66004 and are expressed in 1/10 mm, where the values of x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

2 (amended). The method [Method] as set forth in claim 1, characterized in that the weight percentages x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .



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3 (Amended). The method [Method] as set forth in claim 1 [or 2], characterized in that the quantity of precursor elastomer represents from 1.5% to 20% of the weight of the bituminous matrix.

4 (Amended). The method [Method] as set forth in [one of claims 1 through 3] claim 1, characterized in that the non oxidized bitumen, entering in the making of the bituminous matrix, consists of one single bitumen or of a mixture of bitumens taken from among the straight-run bitumens, the refinery bitumens under reduced pressure, the propane or pentane deasphalting residues and viscosity breaking residues.

5 (amended). The method [Method] as set forth in claim 4, characterized in that the non oxidized bitumen is one bitumen or a mixture of bitumens taken from among the straight-run bitumens.

6 (Amended). The method [Method] as set forth in [one of claims 1 through 5] claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make up the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens taken from among the blown bitumens and the semi-blown bitumens.

7 (Amended). The method [Method] as set forth in [one of claims 1 through 6] claim 1, characterized in that the penetrability of the non oxidized bitumen, used in

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making the bituminous matrix, ranges between 35 and 500 [and especially between 160 and 330].

8 (Amended). The method [Method] as set forth in [one of claims 1 through 7] claim 1, characterized in that the penetrability of the oxidized bitumen, used in making the bituminous matrix, ranges between 20 and 60.

9 (Amended). The method [Method] as set forth in [one of claims 1 through 8] claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make the bituminous matrix, has a ring and ball softening point as defined in the NF standard T 66008, that ranges between 60°C and 120°C.

10 (Amended). The method [Method] as set forth in [one of claims 1 through 9] claim 1, characterized in that the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene, namely butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene.

11 (amended). The method [Method] as set forth in claim 10, characterized in that the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene.

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12 (Amended). The method [Method] as set forth in claim 10 [or 11], characterized in that the copolymers of styrene and of conjugate diene have a styrene content that ranges between 5% and 50% by weight.

13 (Amended). The method [Method] as set forth [in one of claims 10 through 12] claim 10, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range between 10 000 daltons and 600 000 daltons [and preferably between 30 000 daltons and 400 000 daltons].

14 (Amended). The method [Method] as set forth in [one of claims 1 through 13] claim 1, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% [and preferably 1.5% to 20%] of the precursor elastomer and 0.01% to 6% [and more particularly 0.05% to 3%,] of cross-linking agent and/or a functionalization agent while working at temperatures that range between 100°C and 230°C [and preferably between 130°C and 200°C] and under agitation for a period of time of at least 5 minutes.

15 (Amended). The method [Method] as set forth in claim 14, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 100°C and 230°C[, preferably between 130°C and 200°C] and under agitation for a period of



17 (Amended). The method [Method] as set forth in claim 16, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 100°C and 230°C, [preferably between 130°C and 200°C,] and under agitation for a period of time from 5 minutes to 8 hours, [namely from 30 minutes to 6 hours,] to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or functionalization agent and holding it all under agitation at temperatures that range between 100°C and 230°C, [preferably between 130°C and 200°C] and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from 5 minutes to 5 hours, [more particularly between 10 minutes and 180 minutes,] to form the cross-linked and/or functionalized bitumen/polymer reaction product.

18 (Amended). The method [Method] as set forth in [one of claims 14 through 17] claim 14, characterized in that the functionalized elastomer is created within the bituminous matter using a functionalization agent[, namely a functionalization

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agent taken from among the] selected from the group consisting of carboxylic acids or esters bearing thiol or disulfide [groupings] groups and [or from among the] thiolcarboxylic acid polyesters.

19 (Amended). The method [Method] as set forth in [one of claims 1 through 18] claim 1, characterized in that the elastomer is functionalized and [in that we incorporate] one or several reactive additives likely to react with the functional groupings of the elastomer are incorporated into the functionalized bitumen/polymer composition during its preparation where the quantity of the reactive additive(s) ranges from 0.01% to 10% [and more particularly from 0.05% to 5%] of the weight of the bitumen present in the composition.

20 (Amended). The method [Method] as set forth in [one of claims 14 through 17] claim 14, characterized in that the cross-linked elastomer is created within the bituminous matrix, using a cross-linking agent[, namely a cross-linking agent of the] selected from the group consisting of sulfur donor cross-linking [agent type of the] agents and peroxidized [compound type] compounds that generate[s] free radicals at temperatures ranging between 100°C and 230°C.

21 (Amended). The method [Method] as set forth in [one of claims 1 through 20] claim 1, [characterized in that we incorporate] further incorporating one or several additional polymers that are different from the precursor elastomer to the cross-linked and/or functionalized bitumen/polymer composition in an overall

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quantity that ranges between 0.3% and 20% [and preferably between 0.5% and 10%] of the weight of the bitumen of said compositions.

22 (Amended). [Application of the compositions obtained by the method as set forth in any one of claims 1 through 21, as bituminous binders that can be used immediately or following an aqueous emulsion, to make pavements and in particular] A road surface pavement[s, namely of the top coating type, for the making of coated materials that are spread when hot or cold,] or [alternatively for the making of] a watertight facing[s] made from a cross-linked and/or functionalized bitumen/polymer composition made from the method of claim 1.

**Claims 23-28 are added as new claims.**



## ABSTRACT

Compositions produced by forming a homogenous mass consisting of a bitumen matrix wherein a cross-linked and/or functionalized elastomer produced in situ from a precursor elastomer is dispersed in a uniform manner and makes up 0.5 - 30% of the weight of the bitumen matrix. The bitumen matrix is created by associating 95 % - 20 wt. % non oxidized bitumen having a penetrability of 20-900 and 5-80 wt. % oxidized bitumen having a penetrability of 10-90. The compositions can be used as bitumen binders in the production of coverings.

10/018790  
Res'd PCT/PTO 01 OCT 2002

## METHOD FOR PREPARING CROSS-LINKED AND/OR FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND THEIR APPLICATION IN THE MAKING OF PAVEMENTS

The invention relates to a method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a very low susceptibility to temperature. It also relates to the application of said compositions in the making of pavements and, in particular, road surface treatments, coated materials or watertight facings.

We know of the use of bituminous compositions as various top courses and in particular as roadway surface sealing coats provided said compositions have a certain number of essential mechanical characteristics.

These mechanical qualities are valued, in practice, by determining, through standardized tests, a series of mechanical properties, of which the most used are as follows:

- softening point, expressed in °C and determined by the Ring and Ball test defined by the NF standard T 66008,
- brittleness point, or Fraas point, expressed in °C and determined according to the IP standard 80/53,
- penetrability, expressed in 1/10 of a mm and determined according to the NF standard T 66004,
- tensile rheological characteristics determined according to the NF standard T 46002 and in the following quantities:
  - yield stress  $\sigma_s$  in MPa,
  - elongation at yield  $\epsilon_s$  in %,
  - breaking stress  $\sigma_r$  in MPa,
  - elongation at break  $\epsilon_r$  in %.

We can also obtain an indication of the susceptibility to temperature of bituminous compositions from a correlation between the penetrability (abbreviated pen) and the softening point (abbreviated RBT) of said compositions, known under the name PFEIFFER number (abbreviated PN).

This number is calculated using the formula:

$$20 - 500 A$$

$$PN = \frac{1}{1 + 50 A}$$

where A is the slope of a straight line represented by the equation:

$$A = \frac{\log_{10} 800 - \log_{10} pen}{RBT - 25}$$

The bituminous composition's susceptibility to temperature is all the more brittle as the value of the PFEIFFER number is large, or, as the value of the quantity A is smaller, which is the same thing. For refinery bitumens, the PFEIFFER number takes on negative values.

In general, traditional bitumens do not have all the required qualities at the same time and we have known for a long time that by adding various polymers to said traditional bitumens we are able to favorably modify the mechanical properties of the latter and create bitumen/polymer compositions with improved mechanical qualities compared to those of the bitumens alone.

The polymers that are likely to be added to the bitumens are most often elastomers such as polyisoprene, butyl rubber, polybutene, polyisobutene, ethylene vinyl acetate copolymers, polymethacrylates, polychloroprene, ethylene propylene copolymers, ethylene propylene diene terpolymers (EPDM), polynorbornene or alternatively random or block copolymers of styrene and of a conjugated diene.

Among the polymers added to the bitumens, the random or block copolymers of styrene and of conjugated diene and alternatively of styrene and of butadiene are particularly efficient as they dissolve easily in the bitumens and provide them with excellent mechanical and dynamic properties and namely very good viscoelasticity properties.

We also know that the stability of bitumen/polymer compositions in which the polymer added to the bitumen is an elastomer, namely a copolymer of styrene and of conjugated diene such as butadiene, can be improved by reactions, done in situ, of chemical coupling of the polymer with the bitumen, using a sulfur donor coupling agent (FR-A-2376188, FR-A-2429241, FR-A-2528439 and EP-A-360656), or of functionalization of the polymer using a functionalization agent of the acid or carboxylic









Preferably, the first phase of this second form of implementation is implemented by first putting the precursor bitumen in contact with the non oxidized bitumen, while operating at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, and stirring for a period of time ranging between 5 minutes and 8 hours, in particular between 30 minutes and 6 hours, to form a homogenous mixture, then incorporating the cross-linking agent and/or functionalization agent into said mixture, in an appropriate quantity chosen from among the previously defined ranges for said quantity, and while still stirring it all and keeping it at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time ranging between 5 minutes and 5 hours, more particularly between 10 minutes and 180 minutes, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

The cross-linking agent used in the above-mentioned forms of implementation to form the cross-linked elastomer within the bituminous matrix from the precursor elastomer, may alternatively be a cross-linking agent of the sulfur donor type or a cross-linking agent of the peroxygen compound type that generates free radical at temperatures ranging between 100°C and 230°C.



The crosslinking sulfur donor agent may consist of a product chosen from the group that includes elementary sulfur, hydrocarbyl polysulfides, sulfur donor vulcanization accelerators, mixtures of said products together and/or with non sulfur donor vulcanization accelerators. In particular, the sulfur donor cross-linking agent can be chosen from among the M products that contain, by weight, from 0% to 100% of a CA component consisting of one or several sulfur donor vulcanization accelerators and from 100% to 0% of a CB component consisting of one or several vulcanization agents chosen from among elementary sulfur and hydrocarbyl polysulfides, and the N products, that contain a CC component consisting of one or several non sulfur donor vulcanization accelerators and an M product in a weight ratio of the CC component to the M product that ranges between 0.01 and 1 and preferably between 0.05 and 0.5.

The elemental sulfur likely to be used to make part or all the cross-linking agent is advantageously elemental sulfur and preferably crystallized sulfur in the orthorhombic form and known under the name of alpha sulfur.

The hydrocarbyl polysulfides likely to be used to form a part or all of the cross-linking agent can be chosen from among the various hydrocarbyl polysulfides defined in the French patent FR-A-2528439 and include, by preference, the polysulfides with a formula of  $R_{11} - (S)_p - R_{11}$ , where  $R_{11}$  designates a tertiododecyl, hexadecyl, nonyl, decyl, and  $-(S)_p-$  represents a divalent grouping formed by linking of p sulfur atoms where p is a whole number between 2 and 5.

When the cross-linking agent contains a sulfur donor vulcanization accelerator, the latter can be chosen, in particular, from among the thiuram polysulfides, alkylphenol disulfides and disulfides such as morpholine disulfide and caprolactam N,N'-disulfide, that are mentioned in the European patents EP-A-0360656 and EP-A-0409683.

Also, the non sulfur donor vulcanization accelerators that can be used to create the CC component of the cross-linking agents of the N product type can be sulfur compounds chosen from among compounds such as mercaptobenzothiazole and its derivatives, namely metallic thiolate benzothiazole and most of all the benzothiazolesulfenamides, metallic dithiocarbamates and thiuram monosulfides that are defined in the European patents EP-A-0360656 and EP-A-0409683.

Other non sulfur donor vulcanization accelerators, that do not belong to the families defined above, can also be used to create the CC component. Such vulcanization accelerators can be such as diphenyl-1,3 guanidine, diorthotolylguanidine and zinc oxide, where the latter compound may be used in the presence of fatty acid.

Due to its composition, as indicated above, the sulfur donor cross-linking agent can be of the single component type or the multiple component type, where the cross-linking agent of the multiple component type can be created prior to its use or alternatively produced in situ in the environment in which it must be present. The pre-created cross-linking agent of the multiple component type or of the single component type or the components of the multiple component type cross-linking agent created in situ can be used as they are, for example in a molten state, or in a mixture, for example in a solution or in suspension with a diluent, for example a hydrocarbon compound.

The peroxidized compound that generates free radicals at temperatures ranging between 100°C and 230°C, that can be used as a cross-linking agent to produce the cross-linked elastomer within the bituminous matrix, can be chosen, namely, from among the dihydrocarbyl peroxides such as, for example, ditertiobutyl peroxide and dicumyl peroxide.

The functionalization agent that is used to produce the functionalized elastomer, preferably within the bituminous matrix, through a reaction with the precursor elastomer, can consist of a product chosen from among carboxylic acids or esters with thiol or disulfide groupings, and in particular from among those of said carboxylic acids or esters that are suggested for this purpose in the WO-A-9714754 document, or from among the thiolcarboxylic acid polyesters, modified or not, and in particular from among those of said polyesters that are suggested for this purpose in the WO-A-9847967 document.

For further details on the implementation of cross-linking or functionalization agents, for the production of the cross-linked or functionalized elastomer within the bituminous matrix, we can refer in particular to the following documents, FR-A-2528439, EP-A-0360656 and EP-A-0409683 as far as the cross-linking agent is concerned, and to WO-A-9714754 and WO-A-9847967 as far as the functionalization agent is concerned, as the content of said documents is incorporated in this description by reference.

In addition to the cross-linked and/or functionalized elastomer, the cross-linked and/or functionalized bitumen/polymer composition as set forth in the invention can also contain one or several additional polymers different from said cross-linked and/or functionalized elastomer, where said additional polymer or polymers are in particular olefinic polymers such as polyethylene, polypropylene, polybutene, polyisobutene, vinyl ethylene/acetate copolymers, ethylene/propylene copolymers, ethylene/acrylate or alkyl methacrylate copolymers, functionalized olefinic polymers bearing epoxy or COOH groupings such as ethylene/acrylate or glycidyl methacrylate copolymers, ethylene/acrylate or alkyl/acrylate methacrylate or glycidyl methacrylate terpolymers and in particular glycidyl methyl/methacrylate ethylene/acrylate terpolymers and ethylene/acrylate or maleic alkyl/anhydride methacrylate terpolymers and in particular maleic butyl/anhydride ethylene/acrylate terpolymers.

The quantity of the additional polymer or polymers in the cross-linked and/or functionalized bitumen/polymer composition can range between 0.3% and 20% and preferably between 0.5% and 10% by overall weight of the bitumen in said composition.

The possible additional polymer(s) are advantageously incorporated in the bituminous matrix when the precursor elastomer is incorporated into said matrix, prior to the cross-linking or the functionalization.

During its making, between 1% and 40% and more particularly between 2% and 30% by weight of the bitumen of a fluxing agent can be added to the cross-linked and/or functionalized bitumen/polymer composition and can consist in particular of a hydrocarbon oil with a distillation range at atmospheric pressure that is determined in accordance with the ASTM standard D 86-67, ranging between 100°C and 600°C and ranging more specifically between 150°C and 350°C. This hydrocarbon oil, which can among others be a petroleum fraction of aromatic nature, a naphtho-paraffin-base petroleum fraction, a paraffin-based petroleum fraction, a coal oil or an oil of plant origin, is sufficiently "heavy" to limit the evaporation when it is added to the bitumen and also sufficiently "light" to be eliminated as much as possible after spreading the bitumen/polymer composition in which it is contained, so as to once again find the same mechanical properties that the bitumen/polymer composition prepared without the use of a fluxing agent has after being spread when hot. The fluxing agent can be added to the

The quantity of the afore-mentioned reactive additive or additives, that is incorporated into the reaction environment to give birth to the functionalized bitumen/polymer compositions, can go from 0.01% to 10% and more particularly from 0.05% to 5% by weight of bitumen present in said reaction environment.

In one form of implementation of the production of the cross-linked and/or functionalized bitumen/polymer composition that uses a hydrocarbon oil such as defined above, as a fluxing agent, the precursor elastomer, the possible additional polymer(s) and,

if so desired, the cross-linking agent and/or the functionalization agent are incorporated in the bitumen in the form of a mother solution of these products in the hydrocarbon oil that makes up the fluxing agent.

The mother solution is prepared by putting the ingredients of which it is made in contact with each other, namely hydrocarbon oil serving as a solvent, precursor elastomer, and if present, additional polymer(s) and cross-linking agent and/or functionalized agent, under agitation, at temperatures that range between 10°C and 170°C and more specifically between 40°C and 120°C, for a sufficient period of time, for example ranging between 10 minutes and 2 hours, to obtain a full dissolution of the polymeric ingredients and the cross-linking agent and/or the functionalization agent in the hydrocarbon oil.

The respective concentrations of the precursor elastomer and, if present, the additional polymer(s) and the cross-linking agent and/or the functionalization agent, in the mother solution, can vary quite largely based, in particular, on the nature of the hydrocarbon oil used to dissolve said polymer ingredients and the cross-linking agent and/or functionalization agent. Advantageously, the mother solution contains a quantity of precursor elastomer that represents between 5% and 40% and more specifically between 10% and 30% of the weight of the hydrocarbon oil. When present in the mother solution, the cross-linking agent and/or functionalization agent, is used in a quantity ranging, in particular, between 0.05% and 15% and more particularly between 0.1% and 8% of the weight of the hydrocarbon oil.

To prepare the cross-linked and/or functionalized bitumen/polymer compositions or the cross-linked and/or functionalized bitumen/polymer concentrates using the mother solution technique, we mix the mother solution that contains the precursor elastomer and, if used, the additional polymers and the cross-linking agent and/or functionalization agent with the bitumen at temperatures ranging between 100°C and 230°C, more specifically between 130°C and 200°C while stirring, this being done, for example, by incorporating the mother solution to the bitumen still being stirred, at temperatures between 100°C and 230°C and more specifically between 130°C and 200°C, then we keep stirring the mixture resulting therefrom and keep it at temperatures ranging between 100°C and 230°C and more specifically between 130°C and 200°C, for example at the temperatures





invention (examples 4 through 7) to evaluate and compare the physicochemical properties.

We worked under the following conditions:

Example 1 (control)

In a reactor held at 180°C and under agitation, we introduced 964 parts of a straight-run bitumen with a penetrability, determined based on the provisions of the NF standard T 66004, equal to 55 and 35 parts of diblock of styrene and of butadiene with a molecular mass by weight equal to 125 000 Daltons and containing, by weight, 25% of styrene and 75% of butadiene. The content of the reactor was then kept at 180°C under agitation for a period of time equal to 2 hours to form a homogenous mass. We then added 1 part of sulfur as a cross-linking agent to said mass and kept the reaction environment so created at 180°C, under agitation, for 2 hours to produce a control cross-linked bitumen/polymer composition.

Example 2 (control):

We prepared a cross-linked bitumen/polymer composition working as described in example 1, using however 948 parts of bitumen, 50 parts of the diblock copolymer of styrene and of butadiene and 2 parts of sulfur.

Example 3 (control):

We prepared a cross-linked bitumen/polymer concentrate working as follows:

In a reactor held at 180°C and under agitation, we incorporated 15 parts of a resin acid that contained 50% of active matter, to 863 parts of a straight-run bitumen whose penetrability was determined as set forth in the provisions of the NF standard T 66004, equal to 190 and kept the mixture so obtained at said temperature for 20 minutes.

Still working at a temperature of 180°C, we then incorporated, under agitation, 120 parts of a diblock copolymer of styrene and of butadiene identical to that used in example 1 to the bitumen and resin acid mix. The content of the reactor was then kept at 180°C under agitation for a period of time equal to 2 hours to produce a homogenous mass. To said mass we then added 2 parts of sulfur, as a cross-linking agent, and kept the reaction environment thus created at 180°C, under agitation, for 2 hours to produce a control cross-linked bitumen/polymer concentrate. Said concentrate had a penetrability of 96, a ring and ball softening point of 84°C and a Pfeiffer number of 6.85.



We then diluted said concentrate with a straight-run bitumen with a penetrability of 27 and a ring and ball softening point (RBT) of 58.5°C, while mixing for 20 minutes, at 180°C and under agitation, 30 parts of the concentrate and 70 parts of the straight-run bitumen, to obtain a diluted cross-linked bitumen/polymer composition that contained 3.6% of cross-linked block copolymer.

Example 4 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer composition working as described in example 1, replacing however the bitumen used with a mixture of 420 parts of a straight-run bitumen, with a penetrability ranging between 180 and 220, and 544 parts of an oxidized bitumen of the semi-blown type, with a penetrability ranging between 20 and 30, and a ring and ball softening point (RBT) ranging between 75 and 85°C.

Example 5 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer composition working as described in example 1, replacing however the bitumens used with a mixture of 617 parts of a straight-run bitumen, with a penetrability ranging between 180 and 220, and 347 parts of an oxidized bitumen of the semi-blown type, with a penetrability of 40 and a ring and ball softening point (RBT) of 100°C.

Example 6 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer composition, playing the role of a concentrate, working as described in example 1, replacing however the bitumen with 923 parts of straight-run bitumen with a penetrability ranging between 180 and 220 and using 75 parts of the diblock copolymer of styrene and of butadiene and 2 parts of sulfur.

We then diluted the concentrate obtained with an oxidized bitumen of the semi-blown type with a penetrability ranging between 20 and 30 and a ring and ball softening point (RBT) ranging between 75 and 85°C. To do so, we mixed said concentrate for 20 minutes, at 180°C and under agitation, with 952 parts of oxidized bitumen, to obtain a diluted cross-linked bitumen/polymer composition that contained 4% of cross-linked block copolymer.

Example 7 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer concentrate, working as described in example 3. Said concentrate had a penetrability of 96, a ring and ball softening point (RBT) of 84°C and a Pfeiffer number of 6.85.

We then diluted the concentrate obtained with a mixture of bitumens made of 75% of a straight-run bitumen, with a penetrability of 27 and a ring and ball softening point (RBT) of 58.5°C and 25% of an oxidized bitumen of the semi-blown type with a penetrability of 40 and a ring and ball softening point (RBT) of 101°C. The dilution was done by mixing 30 parts of said concentrate with 70 parts of the bitumen mixture for 20 minutes, at 180°C under agitation; the diluted cross-linked bitumen/polymer composition obtained contained 3.7% of cross-linked block copolymer.

For each of the compositions prepared as indicated in examples 1 through 7, we determined the following properties:

- penetrability at 25°C (Pen)
- ring and ball softening point (RBT)
- PFEIFFER number (PN)

The results obtained are provided in the following table.

The polymer content of the compositions is expressed in weight percentages of the overall amount of bitumen.

Table

Examples							
Copolymer in the final composition (% of overall bitumen)	3.6	5.3	3.75	3.6	3.6	4	3.75
Oxidized bitumen in the final composition (% of overall bitumen)	0	0	0	56.5	36	50.8	18.4
Pen (1/10 mm)	46	46	35	45	30	58	48
RBT (°C)	61	68	60.5	69.2	80	69.4	63
PN	1.0	2.3	0.29	2.4	3.1	3.1	1.5

In view of the properties in the above table, it seems that:

- replacement of a part of the non oxidized bitumen with oxidized bitumen in the cross-linked bitumen/polymer composition is translated by an improvement of the physical properties of said compositions and in particular by an increase of the ring and ball softening point (RBT) and of the Pfeiffer number, whether the oxidized bitumen is present during the preparation of the cross-linked bitumen/polymer compositions (compare the results in the control example 1 with those of examples 4 and 5 as set forth in the invention) or whether it is only used during the dilution of the cross-linked bitumen/polymer concentrates (compare the results of the control example 3 with those of example 7 as set forth in the invention), to produce the cross-linked bitumen/polymer compositions;

- replacement of a part of the non oxidized bitumen with oxidized bitumen in the cross-linked bitumen/polymer compositions makes it possible, with comparable properties of penetrability, ring and ball softening point (RBT) and Pfeiffer number, to reduce the composition's content of cross-linked polymer (compare the results of the control example 2 with those of the example 4 as set forth in the invention).

## CLAIMS

1 – Method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C and under agitation, we form a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix in which is uniformly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer used in a quantity that ranges between 0.5% and 30% of the weight of the bituminous matrix, where said method is characterized in that we made the bituminous matrix by associating, by weight, x% of a non oxidized bitumen with a penetrability that ranges between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined as set forth the NF standard T 66004 and are expressed in 1/10 mm, where the values of x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

2. Method as set forth in claim 1, characterized in that the weight percentages x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .

3. Method as set forth in claim 1 or 2, characterized in that the quantity of precursor elastomer represents from 1.5% to 20% of the weight of the bituminous matrix.

4. Method as set forth in one of claims 1 through 3, characterized in that the non oxidized bitumen, entering in the making of the bituminous matrix, consist of one single bitumen or of a mixture of bitumens taken from among the straight-run bitumens, the refinery bitumens under reduced pressure, the propane or pentane deasphalting residues and viscosity breaking residues.

5. Method as set forth in claim 4, characterized in that the non oxidized bitumen is one bitumen or a mixture of bitumens taken from among the straight-run bitumens.

6. Method as set forth in one of claims 1 through 5, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make up the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens taken from among the blown bitumens and the semi-blown bitumens.

7. Method as set forth in one of claims 1 through 6, characterized in that the penetrability of the non oxidized bitumen, used in making the bituminous matrix, ranges between 35 and 500 and especially between 160 and 330.

8. Method as set forth in one of claims 1 through 7, characterized in that the penetrability of the oxidized bitumen, used in making the bituminous matrix ranges between 20 and 60.

9. Method as set forth in one of claims 1 through 8, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make the bituminous matrix has a ring and ball softening point as defined in the NF standard T 66008, that ranges between 60°C and 120°C.

10. Method as set forth in one of claims 1 through 9, characterized in that the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene, namely butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene.

11. Method as set forth in claim 10, characterized in that the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene.

12. Method as set forth in claim 10 or 11, characterized in that the copolymers of styrene and of conjugate diene have a styrene content that ranges between 5% and 50% by weight.

13. Method as set forth in one of claims 10 through 12, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range between 10 000 daltons and 600 000 daltons and preferably between 30 000 daltons and 400 000 daltons.

14. Method as set forth in one of claims 1 through 13, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% and preferably 1.5% to 20% of the precursor elastomer and 0.01% to 6% and more particularly 0.05% to 3%, of cross-linking agent and/or a functionalization agent while





130°C and 200°C, and under agitation for a period of time from 5 minutes to 8 hours, namely from 30 minutes to 6 hours, to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or functionalization agent and holding it all under agitation at temperatures that range between 100°C and 230°C, preferably between 130°C and 200°C and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from 5 minutes to 5 hours, more particularly between 10 minutes and 180 minutes, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

18. Method as set forth in one of claims 14 through 17, characterized in that the functionalized elastomer is created within the bituminous matter using a functionalization agent, namely a functionalization agent taken from among the carboxylic acids or esters bearing thiol or disulfide groupings or from among the thiolcarboxylic acid polyesters.

19. Method as set forth in one of claims 1 through 18, characterized in that the elastomer is functionalized and in that we incorporate one or several reactive additives likely to react with the functional groupings of the elastomer into the functionalized bitumen/polymer composition during its preparation where the quantity of the reactive additive(s) ranges from 0.01% to 10% and more particularly from 0.05% to 5% of the weight of the bitumen present in the composition.

20. Method as set forth in one of claims 14 through 17, characterized in that the cross-linked elastomer is created within the bituminous matrix, using a cross-linking agent, namely a cross-linking agent of the sulfur donor cross-linking agent type of the peroxidized compound type that generates free radicals at temperatures ranging between 100°C and 230°C.

21. Method as set forth in one of claims 1 through 20, characterized in that we incorporate one or several additional polymers that are different from the precursor elastomer to the cross-linked and/or functionalized bitumen/polymer composition in an overall quantity that ranges between 0.3% and 20% and preferably between 0.5% and 10% of the weight of the bitumen of said compositions.

22. Application of the compositions obtained by the method as set forth in any one of claims 1 through 21, as bituminous binders that can be used immediately or following an aqueous emulsion, to make pavements and in particular road surface





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(54) Title: METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR FUNCTIONALIZED BITUMEN/POLYMER  
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(54) Titre: PROCEDE DE PREPARATION DE COMPOSITIONS BITUME/POLYMERE RETICULEES ET/OU FONCTION-  
NALISEES ET LEUR APPLICATION A LA REALISATION DE REVETEMENTS

(57) Abstract: The invention relates to compositions which are produced by forming a homogeneous mass consisting of a bitumen matrix wherein a cross-linked and/or functionalized elastomer produced in situ from a precursor elastomer is dispersed in a uniform manner and makes up 0.5 - 30 % of the weight of the bitumen matrix. The bitumen matrix is created by associating 95 % -20 wt. % non oxidized bitumen having a penetrability of 200-900 and 5-80 wt. % oxidized bitumen having a penetrability of 10-90. Said compositions can be used as bitumen binders in the production of coverings.

(57) Abrégé: On prépare ces compositions en formant une masse homogène constituée d'une matrice bitumineuse dans laquelle est dispersé uniformément un élastomère réticulé et/ou fonctionnalisé produit in situ à partir d'un élastomère précurseur, qui est utilisé en quantité comprise entre 0,5 % et 30 % du poids de la matrice bitumineuse. On constitue la matrice bitumineuse en associant, en poids, de 95 % à 20 % de bitume non oxydé, ayant une pénétrabilité comprise entre 20 et 900, et de 5 % à 80 % de bitume oxydé, ayant une pénétrabilité comprise entre 10 et 90. Lesdites compositions sont utilisables comme liants bitumineux pour la réalisation de revêtements.

WO 00/78870 A1

# Declaration and Power of Attorney for Patent Application

## Déclaration et pouvoirs pour demande de brevet

### French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que :

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

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et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée :

☐ a été déposée le \_\_\_\_\_  
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Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

As a below named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR THE PRODUCTION OF CROSS-LINKED  
AND/OR FUNCTIONALIZED BITUMEN/POLYMER  
COMPOSITIONS AND USE OF SAID COMPOSITIONS IN  
COVERINGS

the specification of which is attached hereto unless the following box is checked:

☒ was filed on June 21, 2000  
as United States Application Number or PCT  
International Application Number  
PCT/FR00/01711  
and was amended on \_\_\_\_\_  
\_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

## French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)  
Demande(s) de brevet antérieure(s)

99/07914	France
(Number)	(Country)
(Numéro)	(Pays)

(Number)	(Country)
(Numéro)	(Pays)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande :

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed  
Droit de priorité revendiqué  
Yes/Oui    No/Non

June 22, 1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed)		
(Jour/Mois/Année de dépôt)		

	<input type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed)		
(Jour/Mois/Année de dépôt)		

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status: patented, pending, abandoned)
(Statut : breveté, en cours d'examen, abandonné)

(Status: patented, pending, abandoned)
(Statut : breveté, en cours d'examen, abandonné)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

French Language Declaration

POUVOIRS : je désigne par les présentes tous avocats de SUGHRUE MION, PLLC énumérés sous le Numéro de Client USPTO figurant ci-après comme mes avocats pour poursuivre la présente procédure et traiter avec l'Office des brevets et des marques (*Patent and Trademark Office*) toute affaire en liaison avec celle-ci, reconnaissant formellement que les avocats spécifiques énumérés sous ce Numéro de Client peuvent être modifiés à tout moment, à la discrétion exclusive de Sughrue Mion, PLLC, et demande que toute correspondance relative à la demande soit adressée à l'adresse mentionnée sous le même Numéro USPTO.

POWER OF ATTORNEY: I hereby appoint all attorneys of SUGHRUE MION, PLLC who are listed under the USPTO Customer Number shown below as my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, recognizing that the specific attorneys listed under that Customer Number may be changed from time to time at the sole discretion of Sughrue Mion, PLLC, and request that all correspondence about the application be addressed to the address filed under the same USPTO Customer Number.



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PATENT TRADEMARK OFFICE

Adresser tout appel téléphonique à : (*nom et numéro de téléphone*)

SUGHRUE MION, PLLC  
+1 (202) 293-7060

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Nom complet de l'unique ou premier inventeur		Full name of sole or first inventor Jean-Pascal PLANCHE	
Signature de l'inventeur	Date	Inventor's signature 	Date 24/07/02
Domicile		Residence Gravetan, 38540 Saint Just-Chaleyssin FRANCE	
Nationalité		Citizenship French	
Adresse postale		Mailing Address Same as Residence 	
Nom complet du deuxième co-inventeur, le cas échéant		Full name of second joint inventor, if any Patrick TURELLO	
Signature du deuxième inventeur	Date	Second inventor's signature 	Date 01/07/02
Domicile		Residence Batiment D "Le Grillon" 69340 Francheville FRANCE	
Nationalité		Citizenship French	
Adresse postale		Mailing Address Same as Residence	



<b>Nom complet du troisième co-inventeur, le cas échéant</b>		<b>Full name of third joint inventor, if any</b> Pierre CHAVEROT	
Signature du troisième inventeur	Date	Third inventor's signature	Date 25/6/2
Domicile		Residence	2, Place des Abricotiers 42730 Saint-Martin la Plaine FRANCE
Nationalité		Citizenship	French PRX
Adresse postale		Mailing Address	Same as Residence
<b>Nom complet du quatrième co-inventeur, le cas échéant</b>		<b>Full name of fourth joint inventor, if any</b> Patrice VEGNY	
Signature du quatrième inventeur	Date	Fourth inventor's signature	Date 02.07 2002
Domicile		Residence	6, impasse des Bleuets 69360 Ternay FRANCE PRX
Nationalité		Citizenship	French
Adresse postale		Mailing Address	Same as Residence
<b>Nom complet du cinquième co-inventeur, le cas échéant</b>		<b>Full name of fifth joint inventor, if any</b>	
Signature du cinquième inventeur	Date	Fifth inventor's signature	Date
Domicile		Residence	
Nationalité		Citizenship	
Adresse postale		Mailing Address	
<b>Nom complet du sixième co-inventeur, le cas échéant</b>		<b>Full name of sixth joint inventor, if any</b>	
Signature du sixième inventeur	Date	Sixth inventor's signature	Date
Domicile		Residence	
Nationalité		Citizenship	
Adresse postale		Mailing Address	